CHEMICAL PROBLEMS OF THE DEVELOPMENT OF NEW MATERIALS AND TECHNOLOGIES
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NON-TRADITIONAL SOLUTIONS OF CELLULOSE AND ITS DERIVATIVES AND PRODUCTS OF THEIR TREATMENT

The main achievements of the Laboratory of cellulose solutions and products of their treatment lie in the following fields:

1) the elaboration of new cellulose dissolving processes;
2) the homogeneous synthesis of cellulose derivatives;
3) the elaboration of the incompatible polymer solutions stabilization method;
4) the creation of new film – fabric materials and filtering equipment on their base;
5) the preparation of solid quickly disintegrated drug forms (tablets, granules) using new water soluble cellulose derivative.

1. NEW PROCESS FOR THE PREPARATION OF HYDROCELLULOSE FIBRES WITHOUT CARBON DISULFIDE

For the purpose of cardinal protecting the environment while producing hydrocellulose fibres and films it is necessary to create a new process allowing for the transmission of cellulose into a dissolved condition without using of carbon disulfide. One of the alternatives suggested herein is to use the $ZnCI_2$–H_2O dissolving system, according to which concentrated solutions of cellulose have been recently received. They are suitable for forming of fibres and films with satisfactory physico-mechanical characteristics [1–4].

The Dissolving of Cellulose in Aqueous Zinc Chloride Solutions

It is known that 62–65 % aqueous zinc chloride solutions at the temperature of 65 °C and more dissolve cellulose. When dropping the concentration or temperature of the zinc chloride solution, or increasing the content of salt in the solution more than 70 % (mass), there is only a swelling of cellulose [5]. These properties of concentrated zinc chloride solutions that under certain conditions cause either swelling or dissolving of cellulose, discovered in 1850, served as a basis for a set of practical proposals for their use, namely: for mercerization of cotton, receiving of vulcanized fibre, preparation of spinning solutions, and forming of rayons [6, 7]. But numerous attempts to produce the fibre and film from cellulose solutions in zinc chloride failed because of the strong destructive action of the solvent, that is why zinc chloride aqueous solutions found industrial application in the production of fibre [8]. In 1984 it was announced in Japan that it was possible to

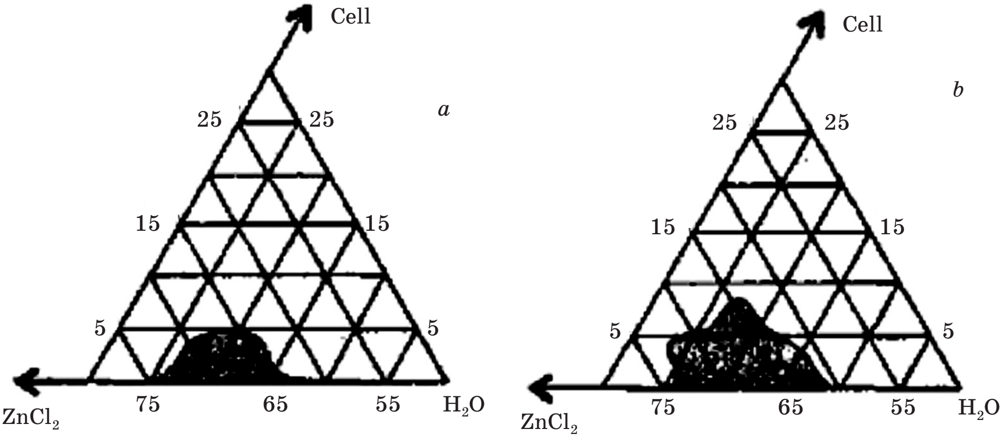


Fig. 1. The diagrams of dissolubility of sulphate cellulose (DP 740)
in the following dissolution conditions:
a) the «direct» method of dissolution: in 65 % $ZnCl_2$ at the temperature of 75 °C;
b) our method [9]: swelling in 80 % $ZnCl_2$ at the temperature of 75 °C for an hour,
dissolution – in 65 % $ZnCl_2$ for 4 hours.

obtain cellulose spinning solutions using cotton from a 67 % $ZnCl_2$ aqueous solution at temperature of 80–105 °C by means of preliminary treatment of the initial material for 5 minutes with zinc chloride solutions concentration being equal or greater than to 79 %. Fibres from the obtained solutions were formed by dry-wet method into the spirituous bath with tensile strength of 13,5 cN/tex and elongation of 18 %.

The suggested method was used for dissolving of high-molecular cotton cellulose and at the time appeared to be worthless for dissolving of wood cellulose, that was widely used in xanthate spinning solution production.

All this predetermined the necessity of carrying out of further experiments in order to find optimal conditions of different kinds of celluloses dissolving in zinc chloride aqueous solutions. The data obtained indicated that, as regards to the immediate influence upon the cellulose of zinc chloride hot aqueous solutions (T > 50 °C), only a limited range of aqueous solutions composition ($ZnCl_2$– 60–73 %) can be considered as the solvent of cellulose. Maximum dissolving capability in regard to cellulose are possessed by 65–68 % zinc chloride solutions at a temperature of 75 °C. But the dissolving of cellulose in them is rather limited and composed, for sulphate cellulose (DP 740), less than 5 % (Fig. la), which is not sufficient for use as a spinning material. Increasing the dissolving time up to 8 or more hours or increasing the temperature of process more than 75 °C brings about a sudden reduction of cellulose DP, but does not allow for increasing the concentration of cellulose in solution. We prepared more concentrated solutions (more or equal to 6 %) by reproducing the method [2], but they did not possess spinning quality due to significant destruction.

For example, the DP of sulphate cellulose (DP 740) precipitated from a 6 % solution was 210. By modifying the conditions of influence of zinc chloride depending on the type of cellulose (cotton, sulphate, hydro-cellulose) we established that the pure cellulose concentrated solutions (C = 6–12 %), keeping DP equal or greater than 300, can only be obtained by means of preliminary treatment by solutions $ZnCl_2$ of non-dissolved composition which allow for implementation of a steady distribution of zinc chloride into the volume of cellulose material. This method was used as a base for all the methods that we suggested for dissolving cellulose [9, 10]. For example, one of the methods [9] provides the activation of cellulose by highly concentrated solutions (the concentration $ZnC1_2$ being greater or equal to 75 %) and consists of following stages: the preparation of a 75–84 % zinc chloride aqueous solution and heating it up to a temperature of 70–80 °C. The insertion of grinded cellulose into the prepared zinc chloride aqueous solution and conducting the process of cellulose swelling for 0.5–2.0 hours at a temperature of 70–80 °C;

Addition of water into the received homogeneous fibrous mass which is necessary for diluting the 75 – 84 % zinc chloride solution to a dissolving composition (63–67 %), reducing the temperature of treatment to 65–75 °C and intense mixing of this mass until it forms a homogeneous viscose-flow solution are the stages of cellulose solution preparation.

For this method of cellulose solution preparation, the diagram of dissolving-sulphate cellulose (DP 740) is given at Fig. 1b. From this diagram it follows that in this case the maximum dissolubility of cellulose is 8,5 %. This 2.0–2.5 times higher than under the direct dissolution of cellulose in 65–68 % $ZnCl_2$ (Fig.la). The importance of using the developed method with regard to different kinds of cellulose is illustrated by the data (Table 1), which show that the maximum concentration of cellulose in the system $ZnCl_2 – H_2O$ defines not only its DP but a set of other factors, including: the origin of cellulose; conditions of delignification; and the degree of structural heterogeneity. The wood celluloses received according to sulphite and sulphate methods possess the best dissolubility in zinc chloride.

Table 1

Several characteristics of the solutions of different kinds of cellulose in zinc chloride and the DP of the fibres moulded from them

Type of cellulose	Max concentration of the cellulose in the solution [%]	Viscosity of 5% solution at 70 °C [Pa/s]	DP initial	DP of the fibre
Sulphate of the Priosersky CPP	8.5	20	740	340
Sulphate Cord	7,0	90	1150	400
Sulphite of the Priosersky CPP	8,0	60	1070	380
Sulphite of the Priosersky CPP	8,0	32	1280	390
Cotton of the Bratsk CPP	7,0	100	1350	390
Cotton of the Svetlogorsk CPP	5,0	110	1000	420
Hydrocellulose	12,0	48	400	300

Table 2

Dependence of DP and viscosity of 7 % sulphate cellulose solution (DP 1070) from duration (F) of storage and temperature (T)

T	F	η	DP	T	F	1	DP
°C	h	Pa·s	–	°C	h	Pa·s	–
70	0	100	380	70	12	12	270
70	0.5	90	370	55	1	210	370
70	1	80	370	39	2	jelly	380
70	2	45	360	20	3	jelly	380
70	3	30	350	20	72	jelly	370
70	8	25	300	20	150	jelly	
70	10	20	280				

Table 3

The influence of calcium chloride on changing the viscosity of 5 % sulphate cellulose solution and its DP in the process of thermostatory solutions at the temperature 75 °C

The time of the thermostatory h	The quantity of calcium chloride (% from mass $ZnCl_2$)					
	0		0.2		0.5	
	DP	η [Pa·s]	DP	η [Pa·s]	DP	η [Pa·s]
0	410	80	440	90	465	105
1	320	26	410	30	420	33
2	300	8	290	14	300	15
4	250	3	260	5	260	5

Their spinning solutions present transparent, viscous liquids. When considering them under a microscope in polarized light it is determined to be no more than 2–3 cellulose fragment and they are according to the main indexes of viscosity, DP cellulose, and concentration of solutions, suitable for further processing into hydrocellulose goods.

The Properties of Spinning Cellulose Solutions in Aqueous Zinc Chloride

Spinning cellulose solutions in zinc chloride with a temperature of preparation of 70 - 75 ˚C have significantly high viscosity 50–100 Pa s, which is rapidly increased when cooling (Table 2). At 18–20 °C 6–9 % cellulose solutions in zinc chloride are converted into transparent thermo-convertible jellies, which after 20–40 hours of storage become dimmed and form regulated supermolecular structures – crystal/solvates with spherulite dimensions from a dozen micrometers up to 1–2 mm. Spherulites have a legibly expressed ring structure, crossed by a cross (Fig. 2). When heating spherulites separated from the original solution in the temperature interval of 45–50 °C, their congrugated melting occurs with a homogeneous transparent solution at which the concentration of cellulose reaches 10 %.

Fig. 2. Spherulites, produced from 5 % solution of sulphite cellulose in aqueous solutions of zinc chloride (x 290)

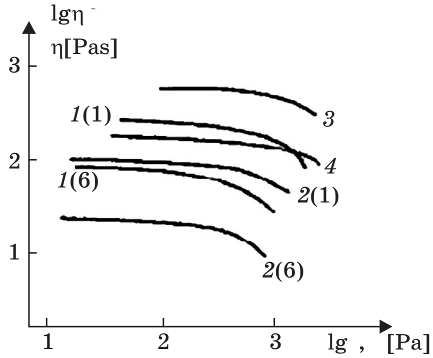


Fig. 3. The flow curves of 5 % solutions of sulphate cellulose in zinc chloride at 50 °C (*1*) and 70 °C (*2*) an the first and sixth days (they are figured in brackets) of their keeping at 20 °C and of 7 % solutions of cotton cellulose at 50 °C (*3*) and 70 °C (*4*).

Research into the stability of spinning cellulose solutions in zinc chloride demonstrated that at temperatures exceeding 70 ^{o}C there is a rapid decrease in viscosity. In spite of this, the spinning solution can not, depending on the kind of cellulose, remain in the increased temperatures for more than 3–8 hours. Otherwise the DP of the cellulose in the solution falls (due to 1, the destruction processes which are especially intensive if the temperature is above 50 °C) to a value lower than 300. This brings about a loss of the fibre - and film - making properties of the solutions. The experiments we have carried out show that the degree of cellulose destruction may be lowered, by the addition to the solution some amount of calcium chloride – about 0.2–0.5 % of the mass of the zinc chloride (Table 3). But at the same time a supplementary rise of the cellulose solution's viscosity takes place, and this is not desirable.

The solution's «life» can be increased owing to a more simple method by keeping the solution made at a reduced temperature (10–20 °C), which delays the destruction processes considerably, and when it is time to mould, by heating the solution to the temperature of viscose-flow condition (T > 50 °C).

The cellulose solutions in zinc chloride are not sensitive to shear deformations and in the area of displacement tensions from 4 to 200 Pa conduct oneself as Newton's liquids (Fig. 3). The rising of the temperature from 50 to 70 °C or maintaining at 18–20 °C practically speaking doesn't influence the flow of the solution.

Taking into consideration these peculiarities of cellulose solutions' conduct in zinc chloride, we determined conditions for moulding fibres and films.

The Moulding of the Hydrocellulose Fibres

The remaking of cellulose solutions into rayons was carried out at the spinning-plants by the wet and dry-wet methods of moulding. The most stable results were carried out by the wet shallow-bath method of moulding using horizontal spinning units.

Table 4

The influence of the coagulation medium composition on the fibres' physical-mechanical characteristics, moulded from 7 % solutions of sulphite cellulose in zinc chloride

Coagulation medium	Temperature of the coagulation medium °C	Tensile strength cN/tex	Elongation %
Ethanol	20	15.8 ± 1,1	7.9 ± 1.7
Ethanol – Water	20	13.2 ± 0.6	10.4 ± 1.3
Ethanol – Water – Zinc Chloride	20	13.6 ± 0.9	12.1 ± 1.1
Isopropanol	35	11.9 ± 0.4	7.5 ± 1.1
Isopropanol – Water	35	14.6 ± 0.7	10.8 ± 0.8
Isopropanol – Water – Zinc Chloride	35	16.8 ± 0.6	13.4 ± 0.5
Ethylene – Glycol – Water	40	14.7 ± 0.5	5.9 ± 0.8
Ethylene – Glycol – Water – Zinc Chloride	40	18.4 ± 1.4	6.0 ± 1.2
Glycerin – Water – Zinc Chloride	40	15.6 ± 0.3	12.8 ± 0.6

It was determined that water-alcohol mixtures have the best coagulation ability for cellulose solutions in zinc chloride. In place of alcohol, ethyl, isopropyl, ethyleneglycol, and glycerine were substituted. The results obtained regarding the influence of the coagulation medium on the properties of the hydrocellulose fibres are set forth in the Table 4. From the data given in the table it follows that both the kind of spirits and their amount in the coagulation bath influence the physical-mechanical characteristics of the fibres. Comparing the properties of the fibres formed in a coagulation medium, which contains ethanol, isopropanol, and ethyleneglycol, one can see that the fibres which were moulded in the water-isopropanol coagulation medium have a better complex of physical- mechanical characteristics (tensile strength and elongation). The pure spirits (ethanol and isopropanol) are sufficient hard precipitates for the cellulose solutions in zinc chloride, and addition to water, which is one of the components of the cellulose solvent, lead to a softening of the coagulation conditions and to the improvement of the entire complex of the fibre's characteristics (strength and elongation). The fibres which were moulded in the coagulation medium containing zinc chloride have much better results as regards physical-mechanical characteristics.

The Table 4 shows that, besides ethanol and isopropanol, the water solutions of ethyleneglycol and glycerin were used, and while moulding into these solutions hydrocellulose fibres were obtained, whose physical-mechanical characteristics are not worse than the those of the viscose fibres.

The analyses carried out regarding the main factors which determine the process of the mould (the speed of the supply of the spinning solution, the speed of receiving, the temperature, and composition of the coagulation medium, etc.) and determination of the parameters of the orientational elongation of the fibre allowed for obtaining hydrocellulose fibres, which are close in their physical-mechanical properties to ordinary viscose fibres of the wool type, and in some characteristics even exceed them. From Table 5, which illustrates a comparison of the properties of the experimental fibres with different types of viscose fibres produced by

Fig. 4. The cros-ssection of the experimental fibre moulded from 6 % solution of sulphate cellulose in zinc chloride (x 730)

industry, one can see that the moulded fibres in the standard conditions have tensile strength from 15 to 25 cN/tex with elongation from 15 to 25 %. The experimental fibres have more strength in the loop (10–13 cN/tex), and are characterized by a high elasticity modulus both when dry and wet (4500–1300 MPa). The diametrical cut of the experimental fibres has a correct round form such as is typical of the diametrical cuts of viscose high modulus and polynose fibres (Fig. 4).

Table 5

The comparative properties of the experimental and different types of viscose fibres

Characterization		Experimental fibre	The viscose fibres			
			Ordinary of the		High Modules	Polynose
			Wool type	Cotton type		
Linear density, tex		0.36–1.1	0.32–0.55	0.17–0.2	0.13–0.17	0.13–0.17
Strength, cN/tex		15–25	16–20	22–25	32–34	36–38
Elongation, %		15–25	21–30	19–24	16–20	3–13
Elasticity modulus, cN/tex		450–1100	150–200	280–300	240–260	–
Strength, cN/tex	when wet	7–10	8–10	11–12	20–22	26–28
	in the loop	12.0–16.0	5.0–6.0	7.0 – 8.0	9.0–9.5	4.5–5.5
Elongation when wet, %		18–27	24–28	24–27	18–24	10–15
Elasticity when wet, cN/tex		45–130	20–30	30–40	80–120	200–250
Solubility in the 6% of NaOH, %		14–16	20–22	20–22	4–8	1,5–3,0
Steadiness to the double pends, thousands of cycles		1.0–2.0	3.0–3.5	30–40	3,0–4,0	–
Swelling in the water, %		110–140	110–120	100–110	65–75	55–65
Water sorption, %		12.5–13.0	12.0–13.5	7.5–8.5	12.5–13.0	11.0–12.0
DP		300–450	280–320	280–320	350–400	450–550

The change of the dissolution and precipitation conditions helped to simplify moulding of the fibres in comparison with method [2], i.e. to exclude the using of the air streak, and to improve the properties of the moulded fibres.

The Production of the Hydrocellulose Films

The production of the hydrocellulose films was realised by sprinkling the cellulose solution in the zinc chloride either on a smooth polished surface or on the reinforced paper layer (in the case of production of reinforced films) with the future regeneration into the coagulation mediums of the different compositions. Table 6 shows that the composition of the medium greatly influences the physical-mechanical characteristics of the films formed, especially their tensile strength. For example, during moulding into an acid coagutation medium, which is also used with the viscose process in the production of cellophane, the tensile strength of the films which are produced by the cellulose solution in zinc chloride is greatly reduced.

The highest tensile strength of hydro - cellulose films is attained when water-spirit mixtures, which contain zinc chloride, are used in the coagulation medium. By means of changing the composition of the mixture «water-spirit-zinc chloride» and the type of the spirits used films were produced which have a strength from 60 to 100 MPa and an elongation from 6 to 9 % without any plastification.

At the same time in the laboratory conditions we have obtained hydro-cellulose films (sausage wrappers) reinforced by paper with a tensile strength of 35 to 60 MPa, moulded in various coagulation mediums. It was established that physico-mechanical properties of reinforced films are determined not only by the composition of the coagulation medium, but also to a considerable degree depend on the properties of the reinforcing material. Sanitary and hygienic tests indicated the nontoxicity of the reinforced films obtained from the aqueous solutions of cellulose in zinc chloride and their applicability for the manufacture or sausage wrappers.

Table 6

The mechanical properties of the films moulded from solutions of sulphate cellulose in zinc chloride

Coagulation medium	Tensile strength MPa	Elongation %
Sulphuric acid – Water	62 ± 8	7.7 ± 0.4
Sulphuric acid – Sulphate of Zinc – Water	33 ± 2	7.3 ± 0.5
Sulphuric acid – Sulphate of Zinc – Sulphate of Sodium – Water	49 ± 3	7.3 ± 0.4
Ethanol	58 ± 18	7.4 ± 1.0
Ethanol – Water	87 ± 13	6.6 ± 0.2
Isopropanol	70 ± 5	7.8 ± 0.5
Isopropanol – Water	80 ±13	8.2 ± 1.2
Isopropanol – Water – Chloride of zinc	96 ± 4	8.4 ± 0.2

The Compatibility of Cellulose and Its Derivatives with Synthetic Polymers in Aqueous Solutions of Zinc Chloride

The use of aqueous solutions of zinc chloride as dissolvent opens up wide-ranging possibilities for the compatibility of cellulose with many synthetic high molecular compounds dissoluble in $ZnCl_2$, as well as for the manufacture of composites possessing the properties of both mixed polymers. We have obtained compatible solutions of cellulose which possess a high kinetic stability with polyvinyl alcohol, polyacrylonitrile and its copolymers, diacetyl-, methoxypropyl, oxyethyl-, diethylaminoethyl-, and phosphate cellulose, Besides, the real dissolubility of polymers in each other is a rather small percentage. For the system of cellulose-alcohol it is, for example, not more than 3–5 %.

We have studied the cellulose - polyacrylonitrile system over a wide scope of compositions (of 5 : 95 to 95 : 5) and have found the order and optimal conditions for the manufacture of compatible solutions. We have also taken rheograms of their viscosity and examined stability of the solutions at various temperatures and time conditions. It was established that a small addition of PAN (5–20 %) to cellulose or, vice versa, an addition of cellulose to PAN, causes a diminution in the first case and an increase in the second of the solutions' viscosity of corresponding initial polymers.

A 1–30 day observation of the solutions of cellulose – PAN, at a temperature of 20–25 °C and in composition 50 : 50 (which is the least acceptable for compatibility) did not reveal any efficient indications of stratification; this fact proves rather kinetic stability of the compatible solutions of cellulose – PAN in zinc chloride. Concentrated compatible solutions, as well as those of cellulose only, were manufactured in laboratory conditions with the use of a spinner. It was established that for solutions with 50 or more percent of cellulose the best coagulation conditions are the following: the coagulation medium - water-isopropyl alcohol-zinc chloride; temperature of coagulation – 35–40 °C. For solutions with a considerable PAN concentration the conditions are as follows: coagulation medium – water – zinc chloride; temperature – 10–15 °C. The fibre moulded in these conditions in the composition of cellulose-PAN with the ratio of 90 : 10 and 10 : 90 has tensile strength and elongation of 15.6 cN/tex, 14 % and 25,2 cN/tex, 32 %, which makes it possible to produce cellulose fabrics modified by PAN addings and polyacrylonitrile fabrics modified by cellulose in the $ZnCl_2 – H_2O$ dissolving system.

A Schematic Diagram of the Process of Obtaining Hydrocellulose Fabrics from Cellulose Solutions in Zinc Chloride

As a result of our comparative examination of concrete technological stages of the viscose and experimental methods, we have proposed a diagram of the process of obtaining hydrocellulose fabrics from cellulose solutions in zinc chloride (Fig. 5). In comparison with the viscose process, the experimental one consists of far fewer technological cycles. It elliminates the stages analogous to those of the first ripening, xanthation, and second ripening; and when finishing the fabric some stages may also be omitted, for example, distillation of carbon disulfide, acidification, and desulphuration. Besides, there is no need of viscose and alkaline drains or damping pits. It makes it possible to considerably diminish the industrial areas and the labor-consuming character of the process. Moreover, the established process is expected to be less harmful owing to a large reduction of toxic fallout in the atmosphere and water basins, due to the exemption of high toxic, in-

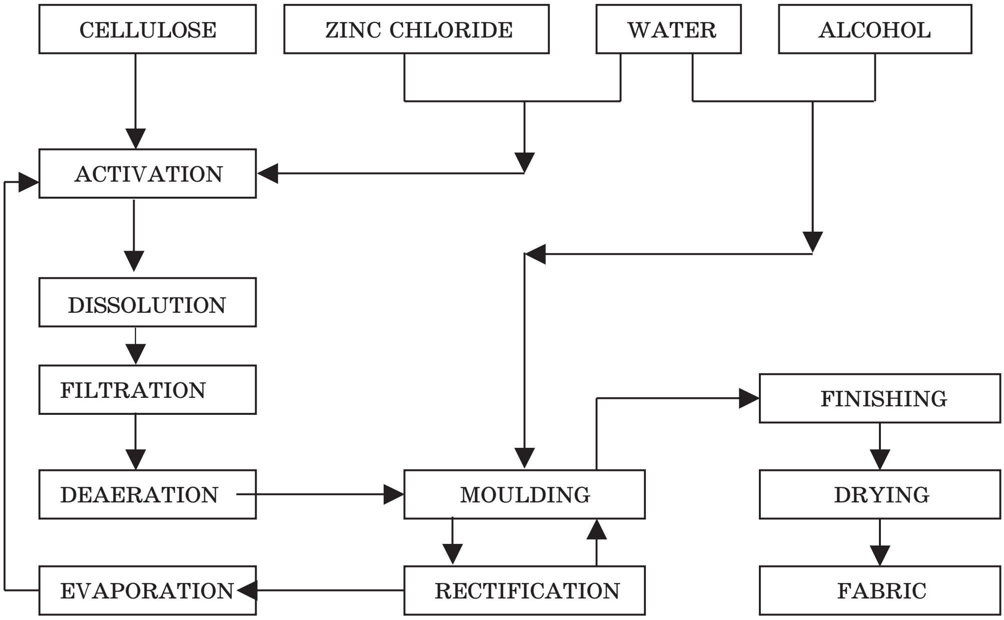


Fig. 5. Schematic diagram of the process of obtaining hydrocellulose fabrics from cellulose solutions in zinc chloride

flammable and explosive carbon disulfide from the practice scheme. The process is also expected to be more economical because of the use of the cheap materials - zinc chloride, alcohols – and due to a reduction of capital equipment expenses and expenditures on environment protection.

A detailed examination of the technological process of regeneration of the primary reagents – which are components of the dissolvent and of the coagulation, - as well as a calculation of the economy of the established process (taking into account the necessity for corrosion-proof equipment usage) reveal the possibility of its industrial implementation and its potential ability to compete with the viscose process.

2. LIQUID CRYSTALLINE PROPERTIES OF HOMOGENEOUSLY SYNTHESIZED NEW CELLULOSE DERIVATIVE

Cellulose derivatives such as hydroxypropyl cellulose; cellulose diacetate, triacetate, and acetate butyrate; etc. are shown to experience the development of an LC order in the arrangement of the anisometric macromolecules in the presence of a relevant solvent when a certain critical polymer concentration is attained; specific values of these concentrations were estimated in [10–17]. Water-soluble sodium salt of cellulose acetate sulfate (Na-CAS) was synthesized via a homogeneous synthesis and prepared as solid transparent and semitransparent plates [18]. The as-prepared Na-CAS is characterized by an exceptionally high water solubility (up to 58 wt %). Highly concentrated aqueous solutions of Na-CAS show stable birefringence. In a stationary state and upon flow, these solutions opalesce, changing their color from yellow-red to violet, which is indicative of the formation of the cholesteric mesophase [11]. To reveal LC ordering in aqueous solutions of the sodium salt of cellulose acetate sulfate we first time performed polarizing microscopic examinations and rheological measurements over its wide concentration range.

As a subject of study we used Na-CAS synthesized according to the procedure described in [18]. The viscosity-average molecular mass M_h of Na-CAS was determined according to the formula [19]

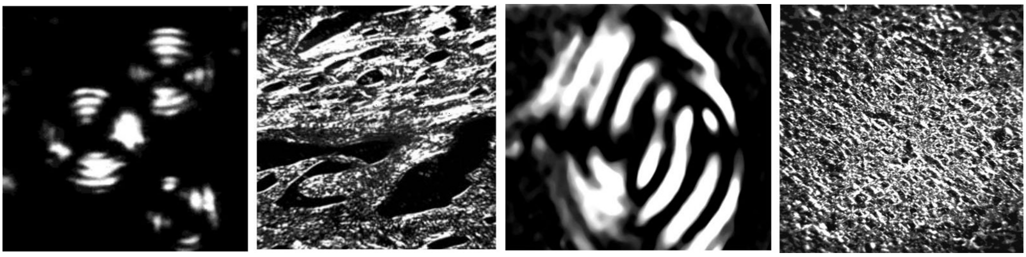
$$[\eta] \quad 2.1 \cdot 10^{\ 3}\,\overline{M}_{\eta}^{0.95}$$

and appeared to be equal $40.5 \cdot 10^3$.

Aqueous Na-CAS solutions with different concentrations varying from 1 to 58 wt. % were prepared at 293 K, taking weighed portions of the compound; the swollen substance was carefully agitated until full homogenization of the system was attained. Dissolution is considered to be complete when the optical observations with a light microscope showed no fragments of non-dissolved Na-CAS. When the dissolution was accomplished, the resultant Na-CAS solutions (c = 42–58 wt %) were deaerated by evacuation for 2 days. The concentration of the solutions prepared was determined more precisely by the gravimetric method [20]. To detect the isotropic phase-anisotropic phase transition, a drop of the as-prepared solution was placed on a slide and pressed with a cover glass and the thin layer of the solution obtained was examined in a polarized light with an Amplival optical microscope equipped with two polarizers. The structural changes observed were recorded on a photographic film using a photocamera. Rheological studies of aqueous Na-CAS solutions were performed on a Rheotest rotary coaxial-cylinder viscometer (Germany) at temperatures varying from 293 to 323 K at shear rates of (1.6–3.0) 10^3 Pa.

As we found, the aqueous Na-CAS solutions are visually transparent and isotropic at concentrations below 2 wt. % and also isotropic but not transparent in the concentration range 2–42 wt. %, thus indicating the association of macromolecules without any ordering in their arrangement. The fact that the association of macromolecules starts at concentrations above 2 wt. % is also proved by the results of the determination of the crossover concentration in the Na-CAS solutions, which appeared to be equal to 1.93 g/dl.

At a concentration of 42 wt. %, the first indications of the development of ordered supramolecular structures as individual spherulites (Fig. 6*a*) appear; as the concentration is increased to 49 wt. %, these spherulites are organized into spherulite ribbons and more complex structural aggregates. The spherulites formed are characterized by a well-pronounced annular structure cut by a Maltese cross. Upon prolonged staying (for one month) at 278 K, the above solutions experience well-defined separation into transparent and opaque phases. According to the published data [21], these phases may be structurally identified as isotropic and anisotropic phases. The appearance of the two-phase region in the Na-CAS solutions suggests that, first, the development of the Na-CAS mesophase is related to geometric anisotropy of the polymer chain as such, rather than to its conformational changes during concentrating the solution. Second, the transition to the LC state in this concentration range takes place only partially [17]. At higher concentrations (above 52 wt. %), the Na-CAS solution in a structural respect represents an LC matrix which contains small-sized regions of isotropic inclusions (Fig. 6*b*) that completely disappear upon a further inc-



a *b* *c* *d*

Fig. 6. Microphotographs of structures in aqueous Na-CAS solutions with a concentration of (*a*) – 42, (*b*) – 50, (*c*) – 52, and (*d*) – 58 wt. %

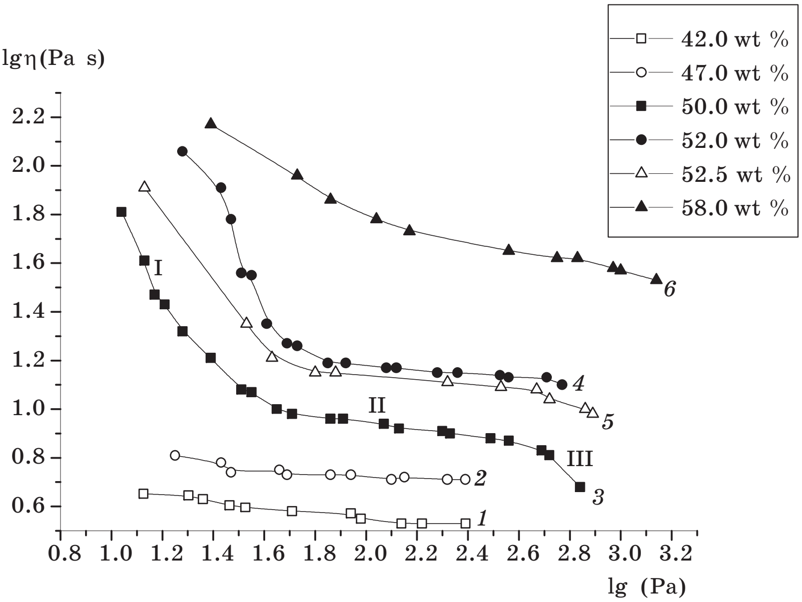


Fig. 7. Viscosity vs. shear stress for aqueous Na-CAS solutions with a concentration of 42.0 – (*1*), 48.0 – (*2*), 50.0 – (*3*), 52.0 – (*4*), 52.5 – (*5*), and 5.08 – (*6*)

rease in the concentration of the solution up to its maximum attainable level (to 58 wt %), the above inclusions. In this case, the corresponding microscopic images of the solution show a confocal texture (Fig. 6*d*) which, upon shearing of the cover glass, is transformed into a planar structure. Furthermore, a specific fingerprint texture typical of cholesteric liquid crystals is observed in the concentration range 50–52 wt. % (Fig. 6*c*).

It is known [21] that the LC nature of polymer solutions is also proved, in addition to their optical properties, by characteristic rheological properties, such as the existence of the yield point and by the absence of the region of constant viscosity in rheological curves.

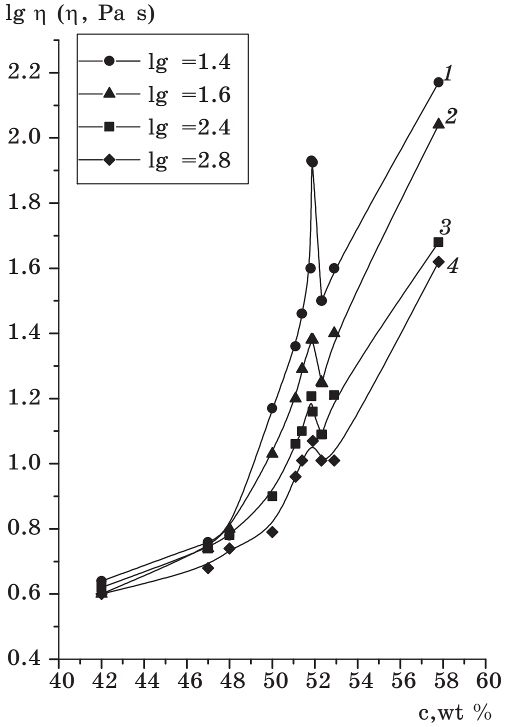


Fig. 8. Viscosity vs. concentration for aqueous Na-CAS solutions at 293 K and at a shear rate of 25 – (*1*), 40 – (*2*), 250 – (*3*), and 660 – (*4*) Pa

For the Na-CAS solutions at the concentrations corresponding to the development of an LC phase, the rheological curves (Fig. 7) show all the aforementioned specific features of LC systems: the region of a marked decrease in the viscosity at low shear stresses (I), a quasi-Newtonian region (II), and the structural wing (III) corresponding to a molecular flow with flow orientation (curves 3–6). The transition to the fully anisotropic solution (c = 58 wt. %) is accompanied by the disappearance of the third region in the flow curve, that is, the structural wing is absent. At the same time, as follows from Fig. 2, the Na-CAS solutions with a concentration of 42 or 47 wt. % show anomalous viscous behavior upon shear deformation, which is typical of structured systems.

The concentration dependence constructed for the viscosity of the Na-CAS solutions from the rheological data shows a maximum typical of LC systems, at a concentration of 52 wt. % (Fig. 8). As the temperature increased from 293 to 323 K, this maximum was shifted to 52.5 wt %. The height of the maximum tends to decrease with increasing the shear deformation rate, thus suggesting the breakdown of LC domains in the Na-CAS system under such external action on the system and the spontaneous ordering of Na-CAS macromolecules in the solutions in the absence of the external action. The ascending branch of the log η = f(c) plot corresponds to isotropic solutions in which the nucleation of ordered structures commences. The maxi-

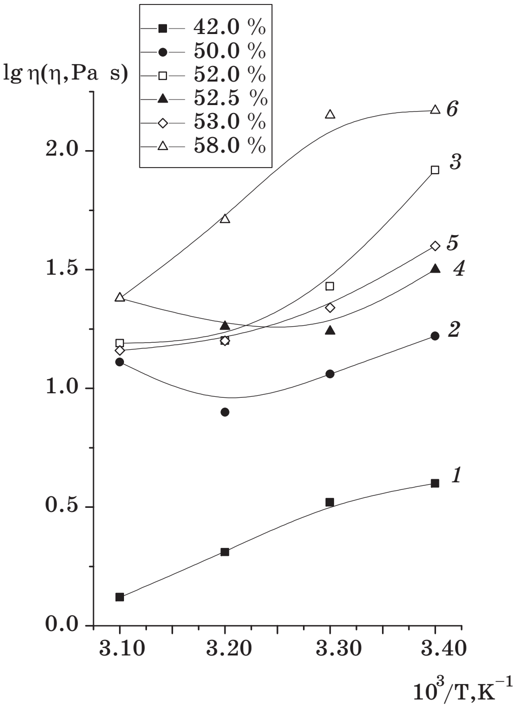


Fig. 9. The effect of temperature on the viscosity of aqueous Na-CAS solutions with the concentration of 42.0 – (*1*), 50.0 – (*2*), 52.0 – (*3*), 52.5 – (*4*), 53.0 – (*5*) and 58.0 – (*6*) wt. %

mum viscosity characterizes the point when the inversion of isotropic and anisotropic phases takes place. The descending branch of the concentration dependence of viscosity describes the behavior of the solutions in which the volume fraction of the isotropic phase dramatically decreases. At a concentration of 52.5 wt % and higher, the solution is fully anisotropic, and viscosity again increases.

Figure 9 presents the temperature dependence of viscosity for the Na-CAS solutions of different concentrations. In a single-phase system, the viscosity monotonically decreases with increasing the temperature; however the temperature dependence shows an extremum for the two-phase solutions (c = 50 – 52.5 wt. %), a this nonmonotonic pattern was also reported for other LC systems [21]. The minimum in the temperature dependence of viscosity may be explained as follows. As temperature increases, the two competing processes take place, a decrease in the viscosity due to the enhancement of thermal motion and a decrease in the viscosity caused by an increase in the volume fraction of the isotropic phase in the system. When the second process starts to dominate, the viscosity increases again after passing through the minimum.

In summary, the parallel investigation of structural transformations and rheological properties of aqueous Na-CAS solutions over a wide concentration range shows that the new cellulose derivative exhibits spontaneous LC ordering which is realized to the maximum extent at 293–323K at a polymer concentration in the solutions higher than 52–52.5 wt. %.

3. NEW METHOD FOR THE STABILIZATION OF CELLULOSE ACETATE – SYNTHETIC POLYMER BLENDS IN SOLUTION

It is generally known that the incompatibility of most polymer pairs in the solution is rather a rule than an exception. For this reason polymer blends solutions in the common solvent are colloid systems like emulsions but not the real solutions. Two layers are formed as a result of a long storage in such systems after a period of time. The segregation of the polymers in polymer blends solutions on a long storage makes their processing practically impossible with standard equipment and it negatively influences the product properties. Consequently the elevation of polymer 1-polymer 2- solvent systems stability is an urgent issue. The elevation of the kinetic stability by means of modification some physical and chemical characteristics of the systems (temperature, viscosity, copolymer adding and so on) has already been mentioned [22].

A new approach to the problem of the stabilization of incompatible polymer blends solutions is suggested as the result of our investigations [22]. This paper studies some novel experimental results on the stabilization of cellulose acetate (CA) solutions containing synthetic polymers. Polymer blend precipitated from a solution of two polymers in the common solvent is taken as a stabilizing agent. The composition of the solution used for the preparation of the precipitated polymer blend and the composition of the stabilized solution are identical. Then the part of the initial polymers in the stabilized solution is changed by the same quantity of precipitated product. It is possible because the ratio of polymers in the solution is the same as in the precipitated product. The main principles of the stabilization of CA solutions which contain chlorinated poly(vinyl chloride) (cPVC), butadiene-acrylonitrile rubber (BAR) and poly(methylmethacrylate) (PMMA) are discussed. The questions addressed are: is the stabilization realized and what is it affected by? For we understand that the real reason of this phenomenon is not common.

The stabilization effect has been found most conspicuous in the case of 50% content of precipitated blend (PB). There is no elevation of stability in the solution with less than 20 % of PB. Table 7 lists the composition and the kinetic stability of the investigated systems. This data shows that a 50 % increment in PB contents leads to a 2–2.5 time increase in kinetic stability.

Any further increase in PB content decreases the stability of the solution. The most pronounced manifestation of the stabilization effect is observed in solutions containing CA or cellulose, these are polymers with H-bond system.

Apart from kinetics separation we have studied the PB influence on the concentration limit of separation (i.e. total polymer concentration in the solution below which there is no phase separation). The substitution of 50 % of initial polymers by their PB contributes to the increase of concentration limit of separation (Fig. 10).

Table 7

Kinetic stability of polymer blends solutions contained stabilizing agent

Polymer ratio, wt. %	Total polymers concentration, g per 100g of solution	Solvent	Quantity of stabilizing agent, % from total content of polymers	The time it takes for solution to be separated into layers, h
CA-cPVC 70 : 30	6	acetone	0	20 ± 2
			50	42 ± 2
CA-cPVC 50 : 50	12	acetone	0	6 ± 0,5
			10	6 ± 0,5
			25	8 ± 0,5
			35	11 ± 0,5
			50	13 ± 0,5
			70	8 ± 0,5
CA: cPVC 30: 70	12	acetone	0	3 ± 0,2
			50	5 ± 0,2
C: cPVC 50 : 50	6	DMF: N_2O_4 (19:1)	0	24 ± 2
			20	30 ± 2
			50	48 ± 2
CA:BAR 50 : 50	8	DMF	0	33 ± 2
			20	40 ± 2
			40	51 ± 2
			50	57 ± 2
CA:PMMA 50 : 50	15	DMF	0	48 ± 2
			30	56 ± 2
			50	62 ± 2
PMMA:BAR 50 : 50	8	DMF	0	3 ± 0,2
			50	4 ± 0,2

In order to determine the reasons of the observed phenomenon we have studied the influence of individually precipitated polymer (IPP) on the kinetic stability of polymer blends solutions. The total polymer concentration in the investigated solution was 6 % , the percentage of CA and cPVC equaled 50:50 (acetone was taken as a solvent). Four variants of making stabilized solutions have been sampled:

1. 25 % (of total content of polymers in the solution) of individually precipitated CA was taken instead of 25 % of initial (i. e. nonprecipitated) CA.
2. 25 % of individually precipitated cPVC - instead of 25 % of initial cPVC.
3. All amount of CA was taken in the form of individually precipitated CA.
4. All amount of cPVC was taken in the form of individually precipitated cPVC.

The effect of kinetic stability elevation has been found to take place only with the introduction of 25 % of individually precipitated CA (Case 1). If introduced in different quantities, individually precipitated cPVC does not have any pronounced effect on the kinetic stability of solution. Complete substitution of the initial CA for the precipitated CA failed to increase the stability.

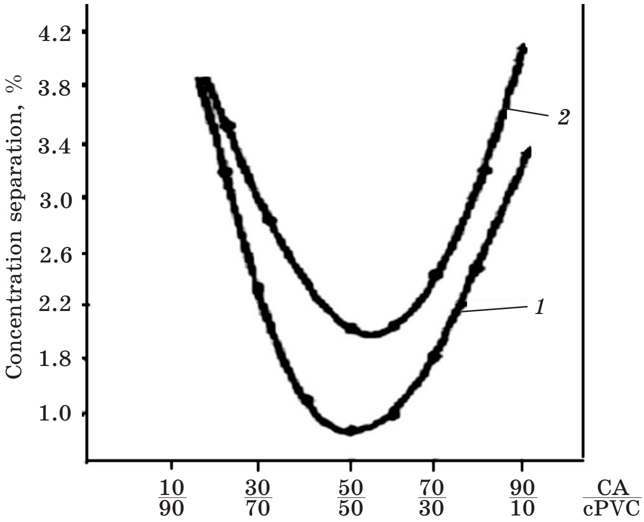


Fig. 10. Concentration separation limit versus polymer relation for the CAcPVC – acetone system.
The region above and under the curse is the region of colloid and true solutions, correspondingly.
1 – initial polemer solution,
2 – solution containing 50 % (by wt.) PB

Three model systems were therefore used for further investigation. These systems were identical as for chemical nature and quantity of polymers (CA : cPVC = 50 : 50 wt. %): 1 – solution of initial polymers blend; 2 – solution containing 25 % of individually precipitated CA; 3 – solution containing 50 % of precipitated CA/cPVC blend.

Influence of Polymers and Solvents Characteristics

The stability of the solutions on the basis of CA with one degree of substitution (DS) but different molecular weights as well as with different DS but the same molecular weight has been studied. Stabilization efficiency was expressed as the ratio of separation time of the stabilized solution to that of the non-stabilized solution. It turned out that the stabilizing effect of CA practically does not depend on the molecular mass but correlates with degree of substitution (DS) for the CA with different molecular weights. It was found that DS increase leads to a lower CA stabilizing effect both in the case of individually precipitated CA and CA simultaneously precipitated with cPVC. By the increment of DS from 2.34 to 2.55 the ratio of separation time decreases from 1.5 to 0.8 in the case of individually precipitated CA and from 1.7 to 1.1 in the case of CA simultaneously precipitated with cPVC.

We have found out that the stabilizing efficiency of CA also varies with the solvent quality (Table 8).

Table 8

The influence of the solvent quality characteristics on kinetic stability of CA:cPVC=50:50 acetone solutions containing 25 % of precipitated CA

The time it takes for the solution (total polymer content is 12 g per 100g of solution) to be separated into layers, h*	Solvent used for CA precipitation	The second virial coefficient A_2 10^{-4} cm^2 mol g^{-2}	Intrinsic viscosity of initial CA in corresponding solvent, dL/g
14 ± 1	acetic acid	9,0	2,15
16 ± 1	DMF	2,7	2,11
18 ± 1	methyl acetate	-	1,97
26 ± 2	dioxan	2,4	1,94
40 ± 2	acetone	0,9	1,84

Thus, the kinetic stability of CA and cPVC blend in acetone did not increase with the introduction of the CA precipitated from the solvent with good thermodynamic quality (acetic acid, DMF, methyl acetate) [24]. However CA precipitated from the worse quality solvents (dioxan, acetone) acts as an efficient stabilizing agent. The worse the solvent quality is, the higher the CA stabilizing efficiency gets (see the correlation between the second virial coefficient A2 and the time of solution separation into layers). From this point of view it becomes clear that the action of simultaneously precipitated blend CA/cPVC is more effective than individually precipitated CA in this case. The solvent quality (in addition to CA) is expected to deteriorate because of the second polymer (cPVC) presence in the solution [25]. As for solvent we also observed the following:

1) The kinetic stability increases when CA precipitated from the solution in DMF added into CA – PMMA blend in DMF and it decreases when the same CA is added into the same blend but in acetone; 2) The stabilizing effect of CA precipitated from the acetone solution disappears when added to the blend of CA-PMMA in DMF, however takes place when added to this blend but in acetone.

We have also established a number of other factors affecting the velocity of solution separation into layers. All these factors have to do with the preparation conditions of the solutions that were used for making the precipitated product. Thus, the elevation of the solution preparation temperature causes the significant lowering of separation velocity. At the same time the elevation of the precipitator temperature acts diametrically opposite. The increase in the polymer concentration in the solution leads to the increase in velocity. To understand the observed phenomenon one has to answer the question: what happens with the polymer during the precipitation from the solution?

It may be expected that the elimination of impurities from the polymer and changing of its chemical composition take place in the precipitation process. However the results of our chemical and spectral analysis showed the identical composition of the initial and the precipitated CA (it is not surprising because of the indifferent character of the used solvent and precipitator). There was no change in the molecular weight distribution of above mentioned CA examples. Thus, Fig. 11 shows the curves of turbidimetric titration of the solutions of the initial and precipitated CA that can give qualitative characteristic of CA polydispersivity.

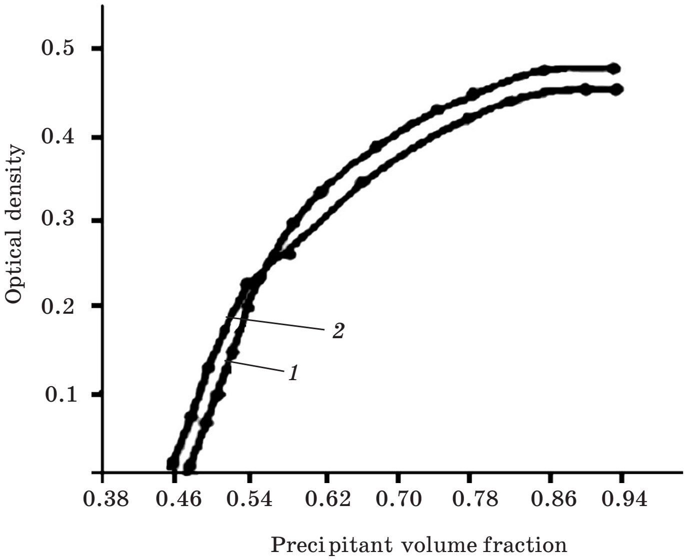


Fig. 11. Turbidimetric titration curves of the initial and precipitated CA solutions. Epichlorohydrin and n – butanol were used as solvent and precipiant

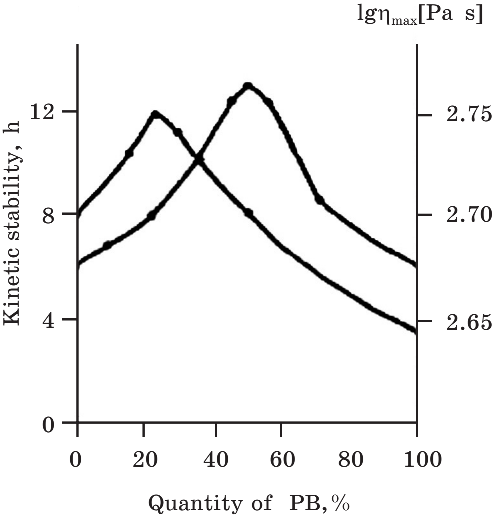


Fig. 12. Kinetic stability (1) and maximum Newtonian viscosity (2) versus PB.

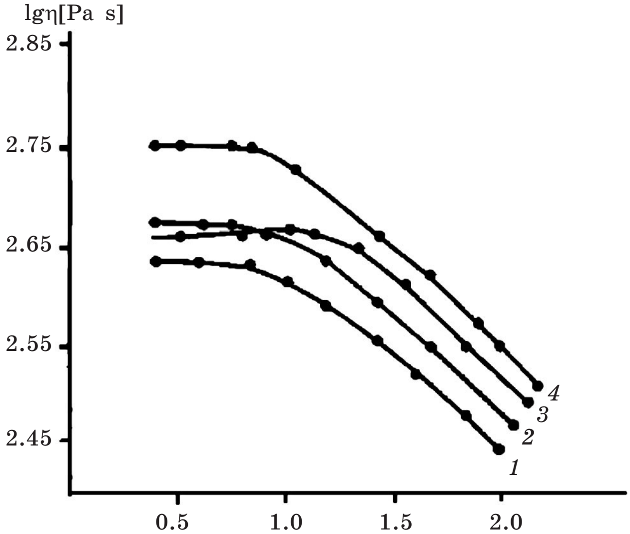


Fig. 13. Viscosity rheograms of CA – cPVC 12 % (total polymer concentration); acetone solutions contained 0 % (*2*), 25 % (*4*), 50 % (*3*) and 100 % (*1*) PB

Moreover, we have attempted to establish the impact of the elimination of different fractions from CA on its stabilizing action. CA without low or high molecular weight fractions has been shown not to demonstrate the stabilizing action. When added to CA/cPVC solution these two samples of CA hasten the separation. Different kinds of CA added to CA : cPVC=50 : 50 solution in DMF could be arranged in sequence according to their capacity to elevate the solutions kinetic stability: $\mathrm{CA}_{\text{without low molecular weight fractions}} < \mathrm{CA}_{\text{without high molecular weight fractions}} < \mathrm{CA}_{\text{simply precipitated}}$.

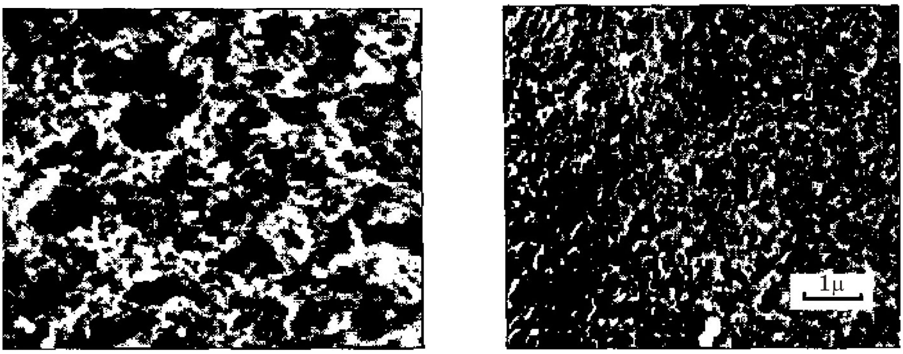
Solutions Rheological Behavior

Our rheological investigations indicated that there is no correlation between the viscosity and kinetic stability of solutions containing different quantities of PB (Fig. 12). The main difference between the rheogram of investigated solution is in the larger extent of maximum Newtonian viscosity region for the solution containing 50 % of precipitated mixture (Fig. 13, curve 3). This fact suggests the change of the solution structure and the parameters of its fluctuated space network. It is to be noted that the increased PB content in the solution leads to the increased activation enthalpy of viscous flow (from 34 to 38 kJ/mol), which presumably implies an increase of intermolecular contact's number.

To establish the correlation between structure and stability of solutions, we have also carried out the work revealing the reasons of solution structure strengthening in the presence of precipitated polymers.

Macromolecules characteristics of precipitated polymers

The results of viscometric investigation of hydrodynamic polymer's characteristics are given in table 3. As follows from these data the decrease of intrinsic viscosity ([h]) and Huggin's constant (kH) of CA takes place during the precipitation process. The characteristics of CA (substitution degree) as well as of the solution, which was used for precipitated products preparation (total polymer concentration, nature of the solvent) influence the value of [h] and kH. There is a corre-



a *b*

Fig. 14. Scanning electron microphotographs of films surface:
a – based on two initial CA solution with different DS;
b – based on the same CA blend + 50% of PB

lation between the hydrodynamic characteristics of macromolecule in dilute solutions and stabilizing action of precipitated polymers in concentrated solutions. Namely the larger the difference between the value of [h] and kH of the initial and precipitated polymer, the more effective the stabilization is.

If it is possible to imagine dissolution of polymer and its subsequent precipitation as inter-and intramolecular bonds «destruction-reduction» process, then the change of temperature, CA substitution degree, solvent nature, second polymer adding into the solution can be considered as factors having affect on the degree of change of hydrogen bonds system.

This is especially true for CA, that has a large number of hydrogen bonds. In particular, the decrease of precipitated polymer [η] is attributable to the fact that macromolecule undergoes destruction or changes the conformation. Since destruction is excluded, we may suggest conformation changing. During the dissolution of CA the solvent destroys part of the hydrogen bonds including intramolecular. This contributes to the increment of the macromolecular flexibility. In this case, macromolecule conforms to a more compact shape. This conformation is fixed during the precipitation. When the precipitated CA is dissolved, macromolecular reproduces this conformation. As seen from the Fig. 14 the morphological structure of the initial and precipitated CA is different. Investigated synthetic polymers (cPVC, PMMA) have not extensive hydrogen bonds system. For this reason, the dissolution and the following precipitation may not practically cause the molecular characteristics change.

IR-spectroscopic Investigation of Solutions

The IR-spectra of initial and precipitated CA powders and solutions, CA-cPVC solutions were recorded in the structure-sensitive region (450……650 cm^{-1}) [26]. As follows from the data (Fig. 15 *a*), the IR-spectra of the powders of the original and precipitated CA have essential distinctions: in the spectrum of precipitated CA the band 432 cm^{-1} vanishes, but the bands 498 cm^{-1} and 455 cm^{-1} shift to 495 cm^{-1} and 450 cm^{-1} respectively. In the IR-spectrum of precipitated CA solution in dimethylformamide (Fig. 15 *b*) the 483 cm^{-1} band vanishes and two bands appear at 495 cm^{-1} and 480 cm^{-1} in the form of two small juts.

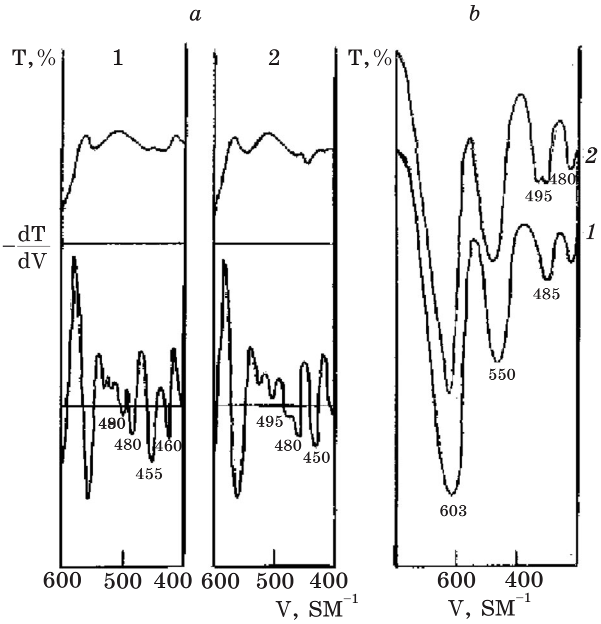


Fig. 15. IR – spectra of the powders (*a*) and solutions (*b*) of the initial CA (*1*) and precipitated CA (*2*)

Though to carry on the assignment of the bands in this area is rather difficult, observed distinctions can be unambiguously connected with the conformation changes of macromolecules.

The results of the theoretical calculations indicate that the oscillation frequency with the participation of acetic groups angles and bonds C – O, C – C, OCO, OCC and also OCO, COC and OCC angles of anhydroglucopyranose links with the participation of oxygen atoms 0 (1), 0 (5) and 0 (4) are exhibited in this region. The considerable mobility of these angles is justified by the significant freedom of the rotation around the C – O bonds compared to C – C bonds and also by the fact that the most mobile atom in the ring is the oxygen atom that has the lowest number of bonds with other atoms. We can assume that in our case the differences between the spectra of original and precipitated cellulose are associated exactly with this phenomenon. The variations of absorption intensity in the pointed region are caused by the variation of relative spatial position of elementary links. In this way, the conformations of precipitated macromolecules turn out to be modified in comparison with conformations of the initial ones. Conformation variations take place obviously on the level of links attachment.

We believe that these conformational changes are induced by the glucopyranosic cycles turning which is caused by the changes intra- and intermolecular hydrogen bonds system of initial CA. All of the preceding makes it possible to assume the macromolecules of initial and precipitated CA differ in hydrodynamic size in the solution. The stabilized solution may be thought of as containing three polymers: initial CA, precipitated CA, which are not conformationally isomorphic and cPVC. We think that this explains the increase of the time of phase separation in the investigated polymer 1 – polymer 2 – solvent systems.

4. NEW FILM – FABRIC MATERIALS AND HIGHLY EFFICIENT FILTERING SYSTEMS ON THEIR BASE

New film-fabric materials, filtering elements and systems produced on their basis are designed for application in food, medical, microbiological, perfumery, cosmetic, chemical, electronic and other industries, besides they can be widely used in agriculture and housing public services.

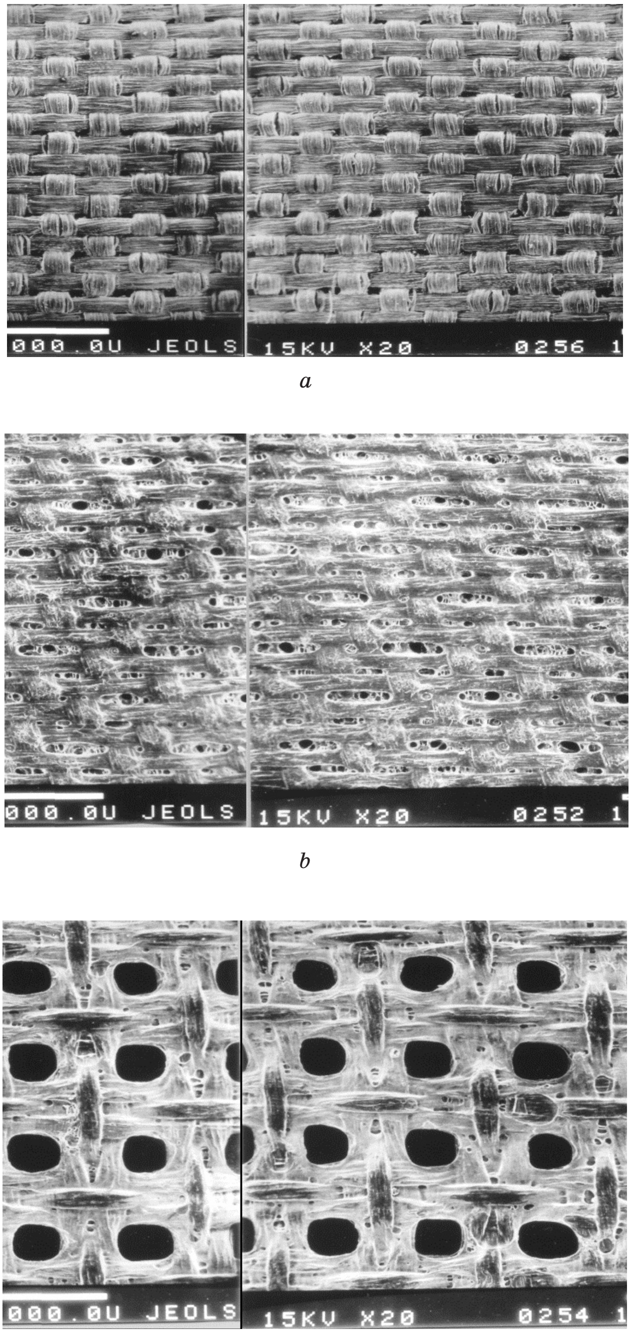
The materials and filtering systems on their base are necessary for purification of large volumes of water and gas from mechanical impurities.

The original technology of production of high-strength film-fabric materials with fixed pore sizes (Fig. 16) hag been developed. Cartridge filtering elements (Fig. 17) with large filtration areas were made up on their basis. Large areas are obtained due to the ability of film-fabric materials for corrugation. Highly efficient filtering systems (Fig. 18) with the capacity of water passage in-between 0.1–40.0 m^3/h were assembled of filtering cartridges. They ensure water purification from sand, mechanical suspended matters and iron oxides (rust) insoluble in water. That is why filters can be used for finishing purification of cold and hot water running along «black» tubes of communal water supply, from artesian wells and other sources. Besides they can be efficiently used in processes of filtration of milk, juices, syrups, drinks, beer, wine materials, liqueurs, vodkas, perfumery and cosmetic liquids, culture media, waste, processing solutions, organic solvents, acids and bases of low and mean concentrations, for gas purification. Filtering systems being offered can be placed on inlet taps of a dwelling-house, porch, fiat, cottage, hospital, kindergarten, canteen, photolaboratory; just before heat meters, meters of cold and hot water, bottle washing machines; bottling lines of liqueurs, vodkas, drinks; milk separators; in systems of preparation of isotonic and hemodialysis solutions; in cooling systems of X-ray apparatuses, etc. New film-fabric materials are applicable for manufacturing of multi-used bag filters for machine milking, fitters for coffee-pots, filters for domestic funnels, filtering sheets in filter presses to keep the washed in layer during beer filtration, etc. In all cases the recovery of initial water passing capacity of filtering sheets and systems is easily achieved by their washing with reverse water flow under pressure.

Unlike the traditionally used filtering fabrics, papers, boards, nonwoven sheets, film membranes, metal nets, ceramic filters etc. new materials posess a unique property – high water permeability and at the same time high retentivity. They are easily regenerated with the recovery of the initial filtering ability. For example, polyether filtering sheet passes through itself more than 180 m^3/sq.m.h of water under the pressure of 0,05 MPa, the effect is 95 % of retained particles with the size of more than 10 micrometres.

New filtering materials are stable to microorganisms, disinfecting solutions, hot water, organic solvents, diluted acids and acids of mean concentration, diluted alkalies: they can stand chemical and temperature sterilization, are easily washed up by water and other detergents – that is why they are reusable.

Both firms-consumers and firms-producers of traditional fitters and filtering elements can be interested in this project.



a

b

c

Fig. 16. Microfotographies of N°TECHMA filtering fabrics: *a* – viscose; *b*, *c* – polyester

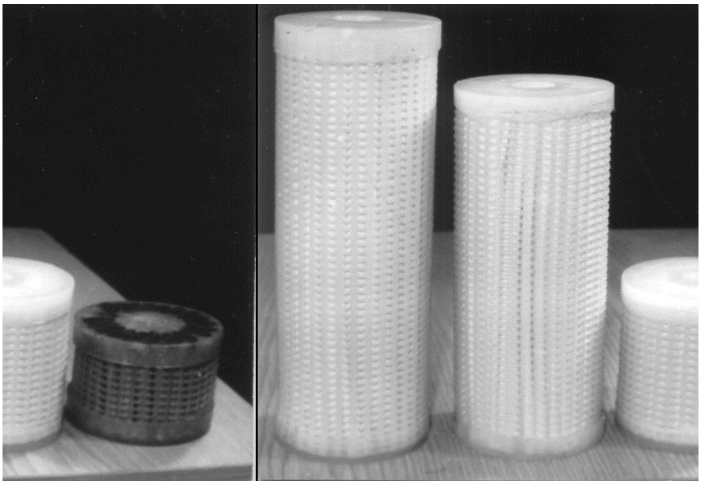
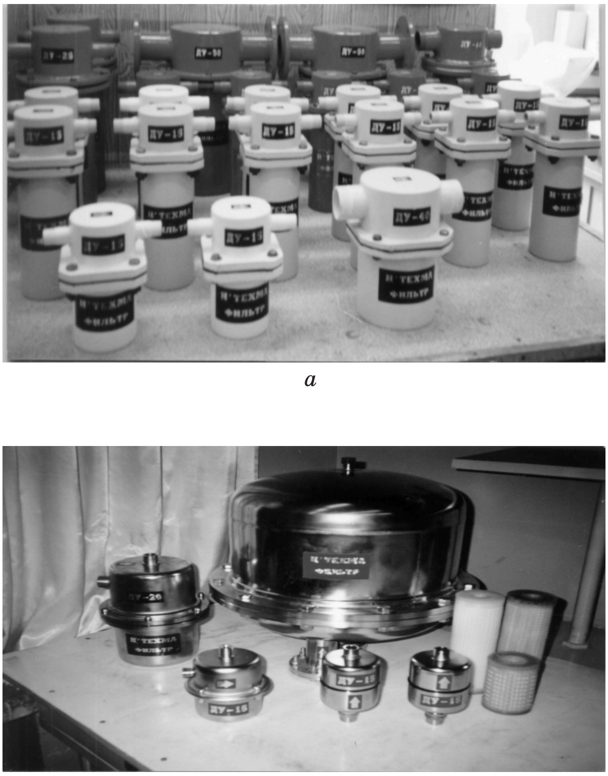


Fig. 17. Filter cartridges



a

b

Fig. 18. N°TECHMA filtering units
of cartridge type (*a*, *b*)

The industrial operation practice for the production of film-fabric materials with specified porosity has been developed. Prototypes of filtering cartridges (filtering elements) and filtering systems with different number of filtering elements (from 1 to 23) have been manufactured and then their approbation in real processes was carried out. There are prototypes for demonstration.

Materials have certificates and resolutions of Belarussian Ministry of Public Health to use them in food industry.

5. NEW ACTIVATED CARBON DRUGS

The reason why active carbon in the form of tablets, granules and capsules cannot be efficiently used as enterosorbent lies within the low stability and flowability of suspensions generated in the gastrointestinal tract of a patient. The nature of the polymer used as a binder while preparing tablets or material for capsule coating should be particularly set off from other factors responsible for the stability and rheology of such suspensions.

The intent of this work was to study the impact of high molecular compounds on the aggregative and sedimentation stability, rheological properties of carbon suspensions in water. Our objective was also to evaluate the possibility of using different polymers for producing drug forms of activated carbon capable of quick disintegration in aqueous media.

The fibrous activated carbon of AUT-MI type was used as activated carbon. Activated carbon was taken in the form of powder, granules or tablets. Industrially produced polyvinylalcohol (PVA) with a molecular mass of $M\mu = 4.4 \cdot 10^6$, polyvinylpyrrolidone (PVP) with $M\mu = 3.0 \cdot 10^5$, starch (S), containing 25 % of amilose and 75 % of amilopectine, polyacrylamide (PAAm) – $M\mu = 4 \cdot 10^6$, polyacrylic acid (PAAc) – $M\mu = 5.0 \cdot 10^5$, carboxylmethyl cellulose sodium salt (NA-CMC) – $M\mu = 5.5 \cdot 10^5$, oxypropylmethyl cellulose (OPMC) – $M\mu = 1.4 \cdot 10^5$, and our new synthesized water-soluble cellulose derivative (WSCD) of polyelectrolyte nature – $M\mu = 3.4 \cdot 10^4$ were used as a binder while making granules and tablets.

Granulates and tablets were prepared on special equipment (mixers, granulators, presses) by mixing the components in the given ratios. The suspensions studied had a dispersed phase concentration of 5–37 mass % and polymer concentration of 8–12 %. Only distilled water was employed as a dispersing liquid since it had earlier been established [27] that aggregative stability and sedimentation velocity are significantly higher in acid (pH 1.6) and alkaline media (pH 8) resembling those of stomach and intestines.

The sedimentation analysis was carried out in compliance with the methods [28]. Rheological studies were conducted using concentric cylinder viscometer Rheotest – 2 with the shearing stress of 1–200 Pa. The concentration of colloid dispersity degree particles that do not form sediment in the period of 30 or more days was determined gravimetrically. The volume of sediments was estimated for the 5 % suspensions (vol. $25 \cdot 10^{-4}$ m^3) in graduated tubes with $1{,}4 \cdot 10^{-2}$ m in diameter after 30 days.

The adsorption activity of carbon drugs in relation to methylene blue that models the class of low molecular toxins with the molecular mass up to 500 Д, was determined by the value of specific adsorption by the procedure [29]. Vitamin B12 adsorption was evaluated by the same procedure.

The interaction velocity of antacid and hydrochloric acid was determined in the following way: 50 mL of 0,1 M HCl solutions were thermostated at 37 ^{o}C within 0.5h, then 0,5g of antacid were added and pH was checked with the help of Thermo Orion PerpHecT Meter (Model 310).

The results of the visual observation and sedimentation analysis showed that the most stable suspensions are formed in the presence of the following polymers WSCD, PVP, Na - CMC, and OPMC.

However the full phase separation, i.e. the formation of transparent water layer and flaky carbon particle sediment, was noted only for suspensions containing PAAm, PAAc, PVA and starch. As for the rest of the suspensions there were sediments on tube bottoms and above there was a fine dispersion of carbon particles. At the same time it turned out that polymers can be arranged according to the value of sediments: WSCD < PVP < Na – CMC ≈ OPMC ≈ carbon suspension < starch < PAAc < PVA < PAAm. The sediment volume changes can be attributed to the change in particle size distribution character in the suspensions. Therefore the increase of sediment volume points at the merger of particles into bigger sets, forming loose flaky residuum, and the decrease indicates the dissociation of particle sets that are generated in the original carbon suspension, and the buildup of thicker sediment. This can also be attested by the results of the sedimentation analysis of granules and tablets suspensions. In the general case WSCD, Na – CMC and OPMC constrict the particle size distribution (PSD), whereas PAAc, PAAm, starch and PVP expand it. Derived curves of particle size distribution for several systems are shown in the Fig. 19. The narrower PSD is achieved through the presence of WSCD in the carbon suspension. The rheological study of features peculiar to aqueous carbon dispersions obtained on the basis of different carbon granulates and original carbon powder showed that dispersions with WSCD as opposed to other polymers behave like a Newtonian fluid. They are also characterized by the absence of structuring in the whole range of the studied dispersed phase concentrations.

In any case, up to the point of 36 % concentration (the further increase of concentration is limited by viscosity growth), structuring is not observed and the dispersions flow evenly (Fig. 20). At the same time structure formation in the dispersion of carbon powder and granules with other polymers starts already in the range of concentrations (Ccr) from 11 % (PAAm) to 21 % (pure carbon). Sudden drop in the viscosity due to the shearing stress increase is evidence to it (Fig. 21, 22). The correlation of Ccr with sedimentation stability allowed to conclude that polymers with Ccr being higher than by pure carbon suspension appear to be flocculants (PAAm, PVA, PAAc, S, MC). Polymers with lower Ccr serve as stabilizers (PVP, WSCD). Whereas with the same polymer content in the suspension the amount of particles incapable of gravity sedimentation is higher in the case of WSCD as compared to PVP. It constitutes 8–9 % and 4–5 % respectively. This implies the bigger specific surface of such suspension and higher adsorption activity of its particles correspondingly.

The obtained results enabled recommendation of WSCD as a unique polymer for creation of different drug forms on the basis of activated carbon.

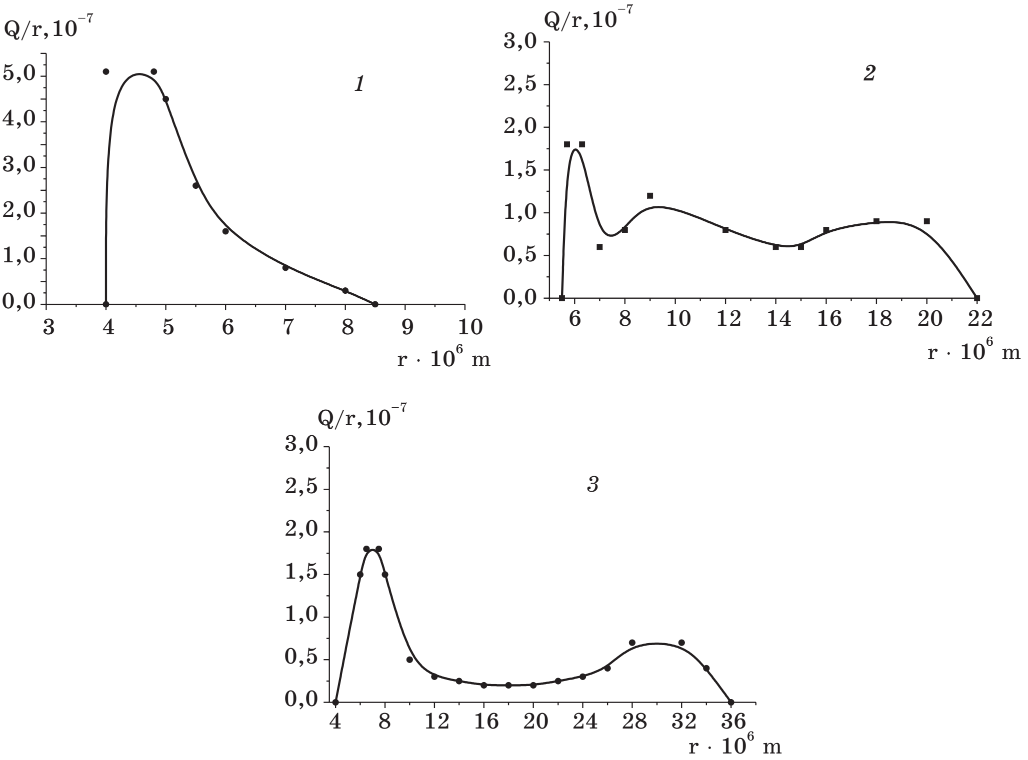


Fig. 19. Derived curves of particle size distribution for the tablets containing WSCD (*1*), starch (*2*) and PVP (*3*)

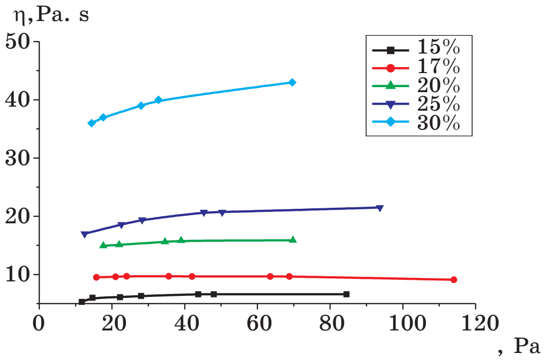


Fig. 20. Viscosity rheograms of aqueous AUT-MI carbon dispersions stabilized by WSCD with different concentrations of the dispersed phase at 37 °C

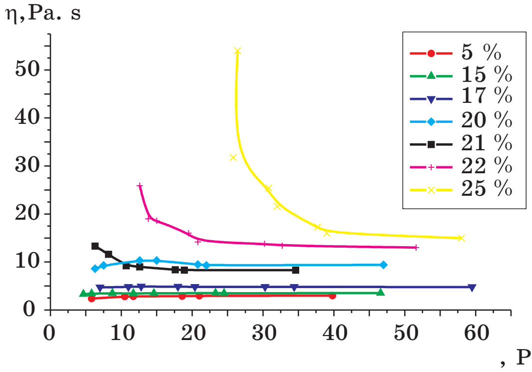


Fig. 21. Viscosity rheograms of aqueous AUT-MI carbon dispersions with different concentrations of the dispersed phase at 37 °C

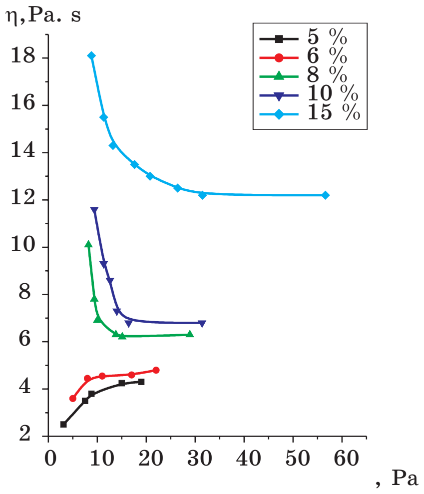


Fig. 22. Viscosity rheograms of aqueous AUT-MI carbon dispersions stabilized by PAA with different concentrations of the dispersed phase at 37 °C

New quickly – disintegrated tablets, new hydrophilic ointments and gels «Carbon-Levomycetin»
«Carbon- Valerian »
«Carbon-Aspirin-Vitamin C»
«Carbon-Aspirin- Vitamin C- Valerian »
«Carbon-Phenygedin »
«Carbon-Nicotinic Acid»
«Carbon-Sodium Nucleinat»
«Carbon-Calcium Carbonate»
«Carbon-Calcium Carbonate-Magnesium Carbonate»
«Carbon-Pectin-Vitamin C-Sweet»
«Calcium Carbonate»
hydrocortisone ointment 1 %
lincomycine ointment 2 %
prednisolone ointment 0,5%
prednisolone gel 0,5 %
dexamethasone gel 0,1 %

Chief distinctions of new tabletted drug forms from the well-known

- the disintegration takes several seconds;
- they do not contain citric add and sodium bicarbonate; while dissolved in water do not carbonate it;
- absence of irritating effect on mucous of gastrointestinal tract and toxic effect on kidneys and liver;
- significant reduction of the administrated dose (in 3–5 times) with the perseverance of the drug efficiency;
- can be used:

– in the form of water solutions for the treatment of children under 4, including infants;

– for bed-patients with the peristaltic dysfunction;

– for patients with stomach and duodenum ulcer.

Main advatages

«Ultrasorb» tablets

«Ultrasorb» tablets disintegrate 10–100 times quicker in contrast to the well-known carbon pills manufactured by Russia, Ukraine, Holland and France. Their sorption capacity is considerably higher regarding harmful substances and their decay products - toxins. This is because of the high specific surface and dispersion degree of the carbon in water solutions of «Ultrasorb» These tablets are suitable for administration: there is no need in chewing, they can be swallowed, taken with water or dissolved in water beforehand. The drug, dissolved in water, is good for the treatment of children including infants. As against powder-like forms of activated carbon like «Belosorb», given tablets do not cause tickles in the throat, belching, retching etc. The course of treatment and the taken dose are decreased several times owing to the high efficiency of the drug- it is also virtual when treating food or medicine allergies, food poisoning. Moreover, what is very important, its high capacity towards the lowering of radio nuclide level in the organism has been revealed (one tablet reduces specific radiation activity by 20 Bq/kg). As compared with such drugs as «Spirulin», «Jablopect», «Medetopect», «Vitus-iodine» traditionally used for these purposes, tablets «Ultrasorb» in terms of mass are several times more active.

«Uglepect» tablets

The combined form of activated carbon and apple pectin is meant to decrease the specific radiation activity of people with advanced radiation dose. It is especially commendable for the children's rehabilitation, as it appears to be a sa vory pastille, containing vitamin C and sweet. What concerns the efficiency of the drug it is comparable with that of the «Ultrasorb».

«Carbon-Aspirin-Vitamin C» («Black Aspirin») tablets

This is a fundamentally new form of soluble aspirin without side effects regarding GIT. Unlike Bayer and UPSA aspirin this one does not contain filling agents such as sodium bicarbonate and citric acid which constitute more than 80 % of the tablet's mass, consequently it doesn't affect stomach and duodenum mucous membrane and the activity of digestive ferments. «Black Aspirin» tablets are 20 times lighter than soluble aspirin.

While using «Black Aspirin» contra-indications are apparently not likely to appear due to the fact that its dissolution does not induce the irritation of stomach mucous membrane, there is no gassing. Children under 4, patients with stomach or duodenum ulcer, can administrate it. Obviously the tablets containing valerian, that reduces GIT spasms, will be particularly beneficial for these kinds of patients.

As opposed to Bayer aspirin, «Black Aspirin» has the same anti-fever effect as the insoluble aspirin. The distinguished advantages of «Black Aspirin» are retained in comparison with traditionally insoluble aspirin tablets, produced by countries here and abroad.

«Carbon-Valerian» tablets

In «Carbon-Valerian» tablets the original valerian extract activity is preserved as against to ordinary 'Valerian extract" tablets. This determines the high efficiency of their usage as a sedative.

«Carbon-Calcium Carbonate-Magnesium Carbonate», «Carbon-Calcium Carbonate» tablets

Calcium and magnesium carbonates are the main representatives of the antacid agents employed to decrease high acidity of gastric juice (under gastritis, stomach and duodenum ulcer). Thanks to the new cohesive used in the tablets, insoluble calcium and magnesium carbonates transfer into fine-dispersed suspension.

They quickly neutralize hydrochloric acid of the stomach contents. By comparison with well-known drugs («Vicair», «Vicalin», «RENNIE») the application of calcium and magnesium carbonates in the combination with carbon allows to sorb carbonic add, evolved during the neutralization of the stomach acid-

This does not evoke stimulating effect on the receptors of the stomach mucous membrane. This also doesn't intensify the secretion of the gastrin and doesn't cause the intensification of the secretion for the second time. They do not contain aluminates.

Main advantages of new ointments and gels

Very high distribution singularity of the acting substance in the volume of the ointment. The degree of dispersion is 15 - 80 mm, that is approximately 5 times higher than in the similar ointments on the fat basis. Ointment-solutions can be made in the number of cases with water-soluble drug substances (lincomycine, prednisolone) or substances that are dissolved in the gel components.

Their penetrating capacity is considerably higher than of those traditional heavy ointments, by reason of their higher compatibility with the organic tissues.

In individual cases when conducting a test of prednisolone ointment it has been found out that its efficacy is so high that there is no need in intra-articuiar injections of prednisolone suspension for the patients with rheumatic arthritis. In addition The new cellulose derivative can be used in order to receipt quick-dissolving tablets that form fine suspensions in the liquid phase without the application of carbon. This is extremely important in the case of receiving quick-acting drug forms, produced from sparingly soluble substances, e. g. «Calcium carbonate».

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